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CO$_2$ ADSORPTION EQUILIBRIA
ON 5A AND 13X MOLECULAR SIEVES
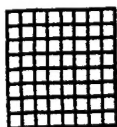# AT ELEVATED CARRIER GAS PRESSURES

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An automated volumetric isotherm system capable of measuring adsorption equilibria of trace levels of contaminants from 1 to 10,000 ppm in carrier gas up to 3.5×10^6 Pa has been developed. The system is a modified version of the volumetric isotherm system previously published by Mahle, et al.[1] The system is used to measure isotherm data for CO_2, a typical contaminant in both separation and purification processes, adsorbed on two commercially available adsorbents, 5A molecular sieve and 13X molecular sieve. These data are measured in the presence of air at pressures of 1.0×10^5 Pa, 5.0×10^5 Pa, 2.5×10^6 Pa, and at temperatures of 278 K, 298 K, and 317 K. Results show that air adsorbed at elevated pressures reduces the amount of CO_2 adsorbed at a given partial pressure and temperature for both adsorbents. The effect of adsorbed air on the CO_2 loading is greater for 5A molecular sieve than for the 13X molecular sieve. Data are correlated using the Dubinin-Radushkevich Equation,[2] which fits the data very well at low pressure but becomes increasingly less representative at elevated pressures.

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PREFACE

The work described in this report was authorized under Contract No. DAAM01-96-C-0043. This work was started in September 1996 and completed in April 1997.

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CO$_2$ ADSORPTION EQUILIBRIA
ON 5A AND 13X MOLECULAR SIEVES
AT ELEVATED CARRIER GAS PRESSURES

1.   INTRODUCTION

In purification systems, the adsorption behavior of low concentrations of a more strongly adsorbed contaminant can be affected by the presence of high pressure carrier and thus adversely affect the anticipated system performance. In separation systems, the more strongly adsorbed contaminant can greatly reduce the separation performance of the adsorbent resulting in low purity product. Contaminant loadings at high pressure are difficult to measure because of the large partition coefficient ratio between the carrier gas and the contaminant. Gravimetric systems using a flow through loading step require large amounts of carrier and still one must distinguish between adsorbed carrier and adsorbed contaminant. Volumetric systems present a problem because the vapor must be circulated at high pressures to achieve equilibrium of the strongly adsorbed contaminant in a reasonable amount of time.

An automated volumetric isotherm system capable of measuring adsorption equilibria of trace levels of contaminants from 1 to 10,000 ppm in carrier gas up to 3.5 x 10^6 Pa has been developed. The system is a modified version of the volumetric isotherm system previously published by Mahle, et al.[1] The system is capable of measuring isotherm data at temperatures between 273 K and 573 K at pressures up to 4.0 x 10^6 Pa. The system is used to measure isotherm data for CO$_2$, a typical contaminant in both separation and purification processes, adsorbed on two commercially available adsorbents, 5A molecular sieve and 13X molecular sieve. These data are measured in the presence of air at pressures of 1.0 x 10^5 Pa, 5.0 x 10^5 Pa, and 2.5 x 10^6 Pa, and at temperatures of 278 K, 298 K and 317 K. Results show that air adsorbed at elevated pressures reduces the amount of CO$_2$ adsorbed at a given partial pressure and temperature for both adsorbents. The effect of adsorbed air on the CO$_2$ loading is greater for 5A molecular sieve than for the 13X molecular sieve. Data are correlated using the Dubinin-Radushkevich Equation[2] which fits the data very well at low pressure but becomes increasingly less representative at elevated pressures.

2.   EXPERIMENTATION

2.1   Apparatus.

An automated volumetric isotherm developed by Mahle, et al.[1] was modified to measure isotherm data for CO$_2$ at elevated carrier (air) pressures. The modified experimental apparatus consists of four subsystems: (1) the main loop circulation system, which consists of the circulating pump, ballast (1000 or 4000 ml), valves, and 316-stainless steel tubing; (2) the temperature-controlled adsorbent bed, which consists of a water bath to control temperatures

below 50 °C and a heater to control temperatures above 50 °C; (3) the chemical injection system, which consists of a series of 3, 6-port Valco valves with loop volumes of 100, 1000, and 10000 µl and was connected to a chemical reservoir; and (4) the vapor-phase analysis system, which consists of a 6-port Valco valve with a 250 or 1000 µl loop to inject samples to a Hewlett Packard Gas Chromatograph Model 5880 with a Thermal Conductivity Detector (TCD) and a 12-foot, 80/100 HayeSep Q column used for the gas-phase analysis. More details of the system are given in Croft, et al.[3]

The most critical modification to the system is the new circulation pump. It is necessary to have a pump which can circulate the vapor at elevated pressures. The pump we chose is a high pressure magnetic pump made by Ruska Instrument Corp. (Model 2330-802). It is capable of delivering flow rates around 200 ml/min at pressures up to 12,000 psi. Although this circulation flow rate is relatively low (typically we use circulation rates on the order of 1-2 lit/min in this system), it is still high enough to allow the system to achieve equilibrium in a reasonable amount of time.

2.2   Materials.

     Adsorbate: $CO_2 < 2$ ppm H_2O
     Bulk Gas: CO_2-free air
     Adsorbents :   W.R. Grace 5A molecular sieve 4x8 mesh
                      W.R. Grace 13X molecular sieve 4x8 mesh

2.3   Procedure.

A fresh adsorbent sample, about 0.30 g to 0.45 g, was weighed from the container vial to get a "wet" adsorbent weight and then inserted into the main circulation system. The entire system was leak-tested prior to each experiment using a standard procedure. The "fresh" zeolite samples were dried and activated *in-situ* at 275 °C for 2 hours with a 2 liter per minute (LPM) dry nitrogen or helium purge to remove any trace water from the zeolite which was adsorbed during the sample weighing process. The system was pressurized using CO_2-free, dry air to the desired isotherm pressure. The system pressure was measured using a 0-1000 psia pressure transducer made by Setra Systems, Inc. (Model # 205-2). After one to two hours, the pressure was checked to determine if any leaks were present.

The same sample is used to measure all isotherm data for each adsorbent. Samples are regenerated *in-situ* at 275 °C for 4 hours, 1 hour with 2 LPM flowing dry nitrogen, and 1 hour with 1 LPM flowing helium or CO_2-free air to remove CO_2 that had adsorbed during the previous experiment. In both heat treatments, samples are taken using a gas chromatograph until no CO_2 and/or water was detectable in the system effluent stream. After completing the flow-through desorption procedure, the adsorbent was cooled to about 150 °C by flowing the pressurizing gas (CO_2-free air) for the isotherm experiment. The appropriate valve is turned to

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put the system into its closed-loop configuration. The gas circulating pump is started and the water bath is turned on to begin to cool the bed to the first desired adsorption temperature. The computer program to control the system and automatically measure isotherm data is then initiated.

3. CORRELATION APPROACH

Adsorption equilibria were correlated using the Dubinin-Radushkevich (D-R) Equation given below.

$$q = q_{max} \exp\left(-\left[\frac{1}{\beta E}\varepsilon\right]^2\right)$$ (1)

where q is the adsorbed-phase concentration (mol/kg), q_{max} is saturation capacity (mol/kg), βE is a fit parameter (kJ/mol), and ε is the adsorption potential defined as

$$\varepsilon = RT\ln\left[\frac{p_{sat}}{p}\right]$$ (2)

where p_{sat} = is the vapor pressure of pure CO_2 at the temperature of interest, T. The gas constant R is (8.31 J/mol K). The saturation pressure was calculated using the modified Miller Equation,[4] given by

$$\ln\left(p_{sat}\right) = p_c\frac{A}{T_r}\left[1 - T_r^2 + B\left(3 + T_r\right)\left(1 - T_r\right)^3\right]$$ (3)

where p_c is the critical pressure of CO_2 (7.39 x 10^6 Pa) and $T_r = T/T_c$ where T_c is the critical temperature of CO_2 (304 K). A and B are constants fit to CO_2 vapor pressure data and are equal to 3.14 and 1.17, respectively.[5] This was used for all temperatures though CO_2 is solid at 303 K and supercritical at 317 K. Even though the D-R Equation is typically used for adsorption on carbon, it provides a useful method to analyze and correlate CO_2 data. Isotherm data at three temperatures are correlated for each adsorbent at each system pressure (6 correlations) by adjusting βE and q_{max} to minimize

$$\sum_{i=1}^{n}\left[\ln(qmeas)_i - \ln(qcalc)_i\right]^2$$ (4)

where qmeas and qcalc are the measured and calculated loadings, respectively, and n is the total number of data points.

4. RESULTS AND DISCUSSION

Shown in Figure 1 and in Figure 2 are the data and the correlation results for CO_2 on 5A and 13X, respectively. Given in the table are the parameter values obtained from the "best-fit" (using Equation 4) D-R Equation for each pressure. These results show that the amount of CO_2 adsorbed is affected by the pressure of air for both adsorbents, 5A and 13X.

Table. Correlation Parameters at Three Total Pressures for CO_2 on Two Different Adsorbents

	CO_2 on 5A Molecular Sieve			CO_2 on 13X Molecular sieve		
Total Pressure (kPa)	1.0×10^2	5.0×10^2	2.5×10^3	1.0×10^2	5.0×10^2	2.5×10^3
ßE (kJ/mol)	13.87	13.30	12.62	15.33	14.93	14.53
q_{max} (mol/kg)	16.08	15.05	10.45	8.89	8.76	6.69

It is clear that the D-R Equation provides a very good method of correlating data at ambient pressure. At ambient pressure, it is likely that the amount of co-adsorbed air is quite low and that it does not adversely affect the amount of CO_2 adsorbed on either adsorbent. However, as the pressure of the air is increased, it appears that the effect of co-adsorbing air is greater for the 5A than for the 13X. This is most evident from the data for CO_2 on 5A at 2.5×10^6 Pa. Not only do these data deviate considerably from the D-R Equation, the higher temperature isotherm data (317 K) is consistently above the 298 K data which is above the 278 K data. This results from temperature affecting the amount of air adsorbed and thus affecting the amount of CO_2 adsorbed. One can see from Figure 1 and Figure 2 that the air pressure affects the CO_2 adsorption because the data begins to deviate from the potential plot as the pressure is increased. This is consistent with the fact that the loading of air will be affected by temperature to a much greater extent than the loading of CO_2 since the heat of adsorption of air is much lower than the heat of adsorption of CO_2. Data measured for 5A molecular sieve at 2.5×10^6 Pa shows higher than predicted (by the D-R Equation) loadings at the highest temperature, 317 K, because the amount of co-adsorbed air is significantly less at 317 K than at 298 K.

Two things are evident relative to co-adsorbed air. First, the effects of air co-adsorption on CO_2 loadings are less for 13X than for 5A. Second, the more that co-adsorbed air affects the amount of adsorbed CO_2, the less the effect that temperature has on the amount of CO_2 adsorbed. This is because as the temperature is increased, the amount of air adsorbed decreases, thus increasing the available adsorption capacity for CO_2.

The correlation parameters in the table provide further insight into the fundamental adsorption behavior for CO_2 on each adsorbent. The parameter, βE, can be used as a measure of the adsorbate-adsorbent interaction energy. From the table, it is evident that the interaction energy between CO_2 and 13X molecular sieve is larger than the interaction energy for

CO_2 on 5A. This is also consistent with the effects of co-adsorbed air previously noted, since a stronger CO_2- adsorbent interaction should reduce the effect of a co-adsorbed species. The behavior of the maximum loading, q_{max}, is also interesting. The saturation capacity of 13X is only about 60% of the saturation capacity of 5A at all three pressures. Thus, the isotherm shape for 5A is more linear over the range of CO_2 partial pressures and temperatures used, but the CO_2 loading at a given partial pressure and temperature is larger for the 5A than for the 13X.

5.   CONCLUSIONS

Three conclusions to be drawn from this effort are:

1.   The isotherm apparatus described here is capable of measuring trace component adsorption equilibrium at elevated pressures.

2.   The effect of air co-adsorption is greater on the 5A molecular sieve than on the 13X molecular sieve.

3.   The adsorption energies for CO_2 on 13X molecular sieve are larger than those for CO_2 on 5A molecular sieve over the range of the data measured here.
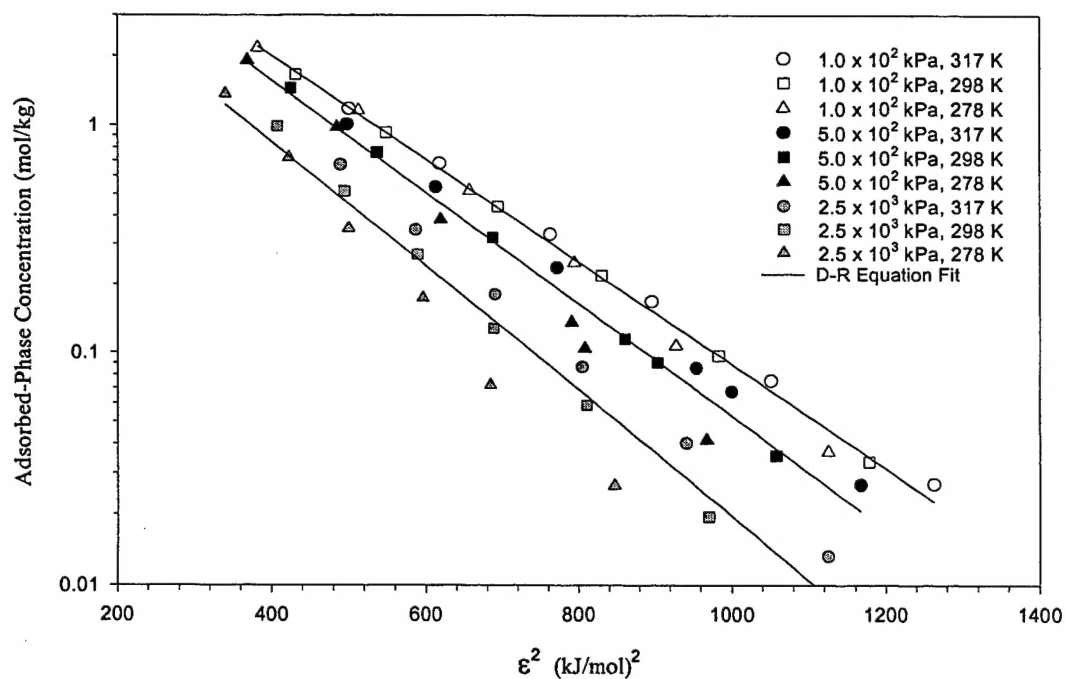
Figure 1. Potential Plot Comparing Measured Data with D-R Fits at Three Pressures for CO_2 Adsorbed on 5A Molecular Sieve
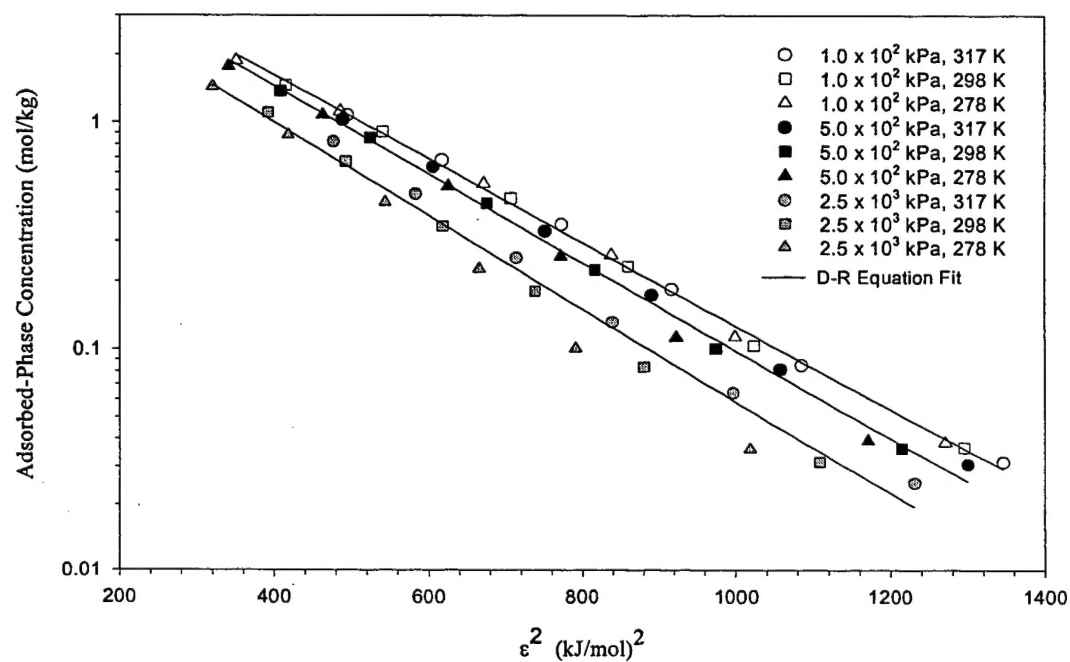

Figure 2. Potential Plot Comparing Measured Data with D-R Fits at Three Pressures for CO_2 Adsorbed on 13X Molecular Sieve

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